



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 144 247
B1**

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 07.03.90

51 Int. Cl.⁵: B 41 M 5/26

21 Application number: 84308504.4

22 Date of filing: 06.12.84

54 Dye-receiving sheets for thermal recording.

38 Priority: 07.12.83 JP 230811/83

43 Date of publication of application:
12.06.85 Bulletin 85/24

45 Publication of the grant of the patent:
07.03.90 Bulletin 90/10

84 Designated Contracting States:
DE FR GB

56 References cited:
EP-A-0 071 169
DE-A-3 303 427
GB-A- 984 216
US-A-3 706 276
US-A-3 933 547

The file contains technical information
submitted after the application was filed and
not included in this specification

73 Proprietor: Matsushita Electric Industrial Co.,
Ltd.
1006, Oaza Kadoma
Kadoma-shi Osaka-fu, 571 (JP)

72 Inventor: Hotta, Shu
8-46, 1-chome Nagaokagu-machi
Hirakata-shi Osaka (JP)
Inventor: Shimizu, Tokihiko
7-17, 6-chome Tatsuta Nishi Ikaruga-cho
Ikoma-gun Nara-ken (JP)
Inventor: Taguchi, Nobuyoshi
5-5, 3-chome Shikanodai higashi
Ikoma-shi Nara-ken (JP)

74 Representative: Myerscough, Philip Boyd et al
J.A.Kemp & Co. 14, South Square Gray's Inn
London, WC1R 5EU (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Description

This invention relates to dye-receiving sheets useful in thermal recording systems utilising a sublimable dye.

5 Duplicating processes involving the thermal transfer of heat-sensitive material are well known. For example, US—A—3706276 describes an image receiving sheet for thermal recording utilising a heat-sensitive transfer material which can be selectively fused upon thermal imaging to a softened condition, the softened material being transferred to the image-receiving sheet to provide an image. The image-receiving sheet is provided with a textured, for example reticulated, wrinkled or cracked, surface thereby to provide a plurality of spaced contacts receptive to the softened heat-sensitive transfer material.

10 Thermal transfer recording utilizing sublimation of dyes is also known and many attempts have been made to utilise such dyes in high speed recording. However, recorded images obtained from such dyes have disadvantages in that they have poor light stability and are low in recording density. These disadvantages are chiefly attributed to insufficient dye receptivity of a color-developing layer of dye-receiving sheets, on which the dyes are deposited or received.

15 The present invention seeks to provide dye receiving sheets for thermal recording utilising a sublimable dye, which sheets can be effectively utilized in high speed recording systems using electronic devices such as thermal heads or laser beam generators and which sheets are capable of providing dye images having good light resistance and high recording density.

20 According to the invention there is provided a dye-receiving sheet for thermal recording utilising a sublimable dye and comprising a support and a color-developing layer formed on the support, said layer being made of a dispersion of inorganic fine particles having a size below 10 μm in a binder consisting of a first resin having functional groups permitting good dye receptivity and a second resin immiscible with the first resin, the volume ratio of said second resin to said first resin being 0.1 to 10:1, whereby microscopic interstices are formed at and along boundaries between the two resins through which dye molecules can pass. The fine inorganic particles in the color-developing layer preferably have an average size as small as below 5 nm (500 Angstrom). Smaller particles are preferred if available. In practice, the preferable size is from 5 to 50 nm (50 to 500 Angstrom).

30 Dye molecules generated from a sublimable dye in a dye layer by application of heat are adsorbed or deposited on the inorganic particles and the dye-receptive resin at adsorption or deposition points or sites of the particles and the dye-receptive resin. These points or sites of the particles and the dye-receptive resin are generically called color-developing points or sites. The second resin which is immiscible with the first dye-receptive resin contributes to increase a density of effective color-developing sites with an attendant increase of recording density as will be more particularly described later.

35 Reference will now be made to the accompanying drawings in which:

Fig. 1 is a schematic view, in section, of a known dye receiving sheet;

Fig. 2 is a schematic, sectional view illustrating the manner of thermal recording using a dye-receiving sheet according to the invention; and

40 Fig. 3 is a schematic, sectional view showing the dye-receiving sheet of Fig. 2 in detail. First, a prior-art dye-receiving sheet of Fig. 1 is described briefly, in which there is illustrated a dye-receiving sheet 1. The sheet 1 has a substrate 2 and a color-developing layer 3 formed on the substrate 2. The layer 3 includes fine particles 4 of an inorganic material dispersed in a resin binder 5. In this known sheet 1, color-developing sites or points 6 are fully covered with the resin binder 5, by which dye molecules 7 sublimated from a dye layer of a dye transfer sheet (not shown) by application of heat from outside of the dye transfer sheet cannot penetrate into the color-developing layer 3. In other words, the dye molecules deposited on or arrived at the surface of the color-developing layer 3 do not substantially contact with the color-developing sites 6 in the layer 3. As a result, the dye molecules not only cannot fully develop a color thereof, but also tend to suffer an influence of an external environment, leading to poor stabilities and particularly poor light resistance. In addition, the dye is deposited only on the outer surface of the layer as an outermost layer, so that the dye image may be readily contaminated with water or oils with a considerable lowering of the image quality.

50 Fig. 2 shows the principle of thermal recording using a dye-receiving sheet according to the invention. In Fig. 2, there is shown a dye-receiving sheet 10 which includes a support 12 and a color-developing layer 14 formed on the support 12 similar to the prior art sheet. The layer 14 is made of fine particles 16 of inorganic materials dispersed in a mixture of two types of resins which are not miscible with each other. One resin has good dye receptivity or good affinity for dyes. In the figure, regions of the respective resins are schematically and roughly depicted as 18 and 18' for the first and second resins, respectively. This mixed resin layer will be described in more detail in Fig. 3.

60 Above the sheet 10 is provided a dye transfer sheet 30 which includes a support 32 and a sublimable dye layer 34 which is provided in face-to-face relation with the color-developing layer 14. When the dye layer 34 is heated in an imagewise pattern by means of, for example, a thermal head 36, dye molecules sublimate according to the imagewise pattern and deposit on color-developing sites on or in the color-developing layer 14 where a color develops.

65 The color development using the color-developing layer 14 is described in Fig. 3 in more detail. In the layer 14 are contained the fine particles 16 dispersed in the resin binder consisting of the regions 18 of the

first resin having good affinity for dyes and the regions 18' of the second resin immiscible with the first resin. Because of the immiscibility of both resins, microscopic interstices 22 are formed in the color-developing layer 14 as shown. This is characteristic of the dye-receiving sheet 10 of the present invention. These interstices permit easy passage or penetration of dye molecules into the layer 14. As a result, the dye molecules can arrive at color-developing sites or points 20 in the color-developing layer 14. This is why the dye-receiving sheet according to invention is highly resistant to light and ensures a high recording density.

The first resin having color-developing sites should have functional groups serving as the sites. Preferably, the first resin should have a solubility parameter not smaller than 9.5 and most preferably not smaller than 10.0. Examples of such resin include polyesters, polyamides, acrylic resins and acetate resins. On the other hand, the second resins immiscible with the first resin. Preferably, the second resin should have a solubility parameter (for a definition of solubility parameter see J. Appl. Chem., 3, February 1953, pages 71 to 79, especially equation (15) on page 74) not larger than 9.0 and most preferably not larger than 8.5. Examples of the second resin include hydrocarbon resins, fluorine resins and silicone resins. Specific examples of the hydrocarbon resins are polyethylene, polypropylene, polystyrene, polybutadiene, styrene-butadiene rubber (SBR) and the like.

These hydrocarbon resins, fluorine resins and silicone resins have substantially no color-developing points or sites. Of these resins, hydrocarbon resins including polyethylene are preferred because they are inexpensive and are tack-free in nature, so that they act to prevent fusion bond between the dye layer 34 and the color-developing layer 14 upon application of heat from the thermal head 36.

In the above arrangement of the dye-receiving sheet of the invention, dye molecules substantially penetrate into the color-developing layer 14 and chemically combine with and/or adsorb on active or color-developing sites of the inorganic particles and the first resin. The disadvantages of the prior art sheet described before can be completely overcome.

Inorganic fine particles dispersed in the resin binder are particles of, for example, silica, alumina, titanium oxide or active clay having a size below 10 μm . Preferably, fine particles of silica, alumina and/or titanium oxide having an average size of below 50 nm (500 Angstrom) are used. These fine particles are so high in density of color-developing points per unit volume that they greatly contribute to increase the recording density.

The ratio by volume of the second resin to the first resin of high dye receptivity should be from 0.1 — 10:1. Outside the range, the effects of the second immiscible resin being mixed with the first resin are lost. The ratio by volume of the fine particles to the total amount of the first and second resins preferably is 0.1 to 10:1. With the ratio below 0.1:1, a satisfactory recording density may not be obtained. On the other hand, when the ratio is over 10:1, the binding effect of the resins is unfavorably impeded.

In order to further improve the light resistance and other stabilities of recorded dye images, known UV absorbers and/or antioxidants may be incorporated into the resin binder.

The support may be made of any materials in the form of sheets or films and include paper sheets, synthetic papers and the like as ordinarily used for these purposes.

The dye receiving sheets of the invention may be especially useful when dye transfer sheets make use of sublimable disperse dyes, basic dyes and/or dye formers. The first resins such as polyesters, polyamides, polyacrylic resins and acetate resins permit dye molecules to be dispersed therein and the inorganic fine particles have the ability of adsorbing dye molecules at active or acidic points or sites thereof. This is why stable and clear images can be obtained using the dye-receiving sheets of the invention.

The present invention is described in more detail by way of example.

Example

Compositions comprising the following three emulsions or dispersions A, B and C in different ratios were prepared and each composition was applied onto a synthetic paper of polypropylene in a thickness of 5 μm by the use of a wire bar, thereby forming a color-developing layer on the paper. The composition was dried to obtain a dye-receiving sheet for thermal recording.

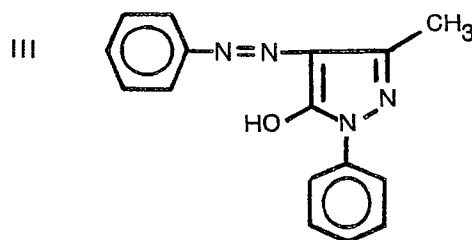
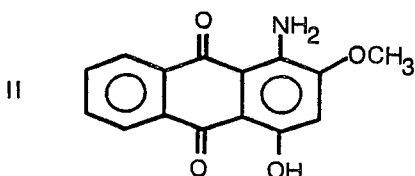
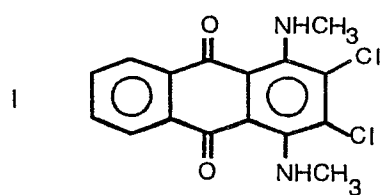
Emulsion A: aqueous emulsion of 20 vol% of polyester (available under the name of Vyrone).

Emulsion B: aqueous emulsion of 20 vol% of polyethylene.

Emulsion C: aqueous dispersion of 20 vol% of silica powder having an average size of 20 nm (200 Angstrom).

On the other hand, dye solutions of 4 parts by volume of each of disperse dyes of the following formulas (I), (II) and (III), 3 parts by volume of polysulfone and 100 parts by volume of monochlorobenzene were prepared. Each solution was applied onto a 12 μm thick condenser paper by the use of a wire bar to obtain a dye transfer sheet for thermal recording.

EP 0 144 247 B1



The dyes of the formulas (I), (II) and (III) are able to develop cyan, magenta and yellow colors, respectively.

These dye transfer sheets and dye-receiving sheets were brought into intimate contact with each other in pairs so that the formed layers face facing each other. Subsequently, a dye image was formed on the dye-receiving sheet by the use of a thermal head. The recording conditions were as follows.

Ligne densities of main and sub scanings: 4 dots/mm

Electric power for recording: 0.7 W/dot

Heating time of the head: 8 milliseconds

The resulting dye images were subjected to measurement of a resistance to sunlight according to the method prescribed in JIS L0841. The ratios by volume of the emulsions A and B and the dispersion C, recording densities of the cyan, magenta and yellow colors and the resistance to sunlight are shown in the following table. The resistance to sunlight is evaluated as five grades of 5, 4, 3, 2 and 1 which, respectively, indicate "Very Good", "Good", "Moderate", "Poor" and "Very Poor".

TABLE

Volume Ratios of Emulsions & Dispersion			Recording Densities			Light Fastness		
A	B	C	Cyan	Magenta	Yellow	Cyan	Magenta	Yellow
9	1	10	1.0	0.8	0.7	3	3	3
7	3	10	1.2	1.0	0.9	4	4	4
5	5	10	1.4	1.2	1.0	4	4	5
3	7	10	1.3	0.9	1.0	4	3	4
1	9	10	1.2	0.8	0.8	3	3	4
7	3	50	1.3	1.2	1.0	4	3	4
5	5	50	1.4	1.2	1.0	3	3	4
3	7	50	1.4	1.3	1.1	3	3	3
7	3	2	1.2	1.1	0.8	4	4	5
5	5	2	1.3	1.1	0.9	4	4	5
3	7	2	1.4	1.0	1.0	4	3	4
10*	0*	10*	0.8	0.7	0.6	2	2	3
0*	10*	10*	1.0	0.7	0.7	2	1	2

* Comparison

EP 0 144 247 B1

The above procedure was repeated except that aqueous solutions or emulsions of polymethyl methacrylate, acetyl cellulose and water-soluble polyamide were used as the emulsion A, an SBR latex was used instead of the emulsion B, and an aqueous dispersion of active clay powder having an average size of 1 μm or an aqueous dispersion of alumina or titanium oxide powder having an average size of 30 nm (300 Angstrom) was used instead of the dispersion C. The resulting sheets were capable of yielding images having recording densities of cyan, magenta and yellow of over 1.0, and 0.8 and over 0.6, respectively, and a light fastness over 3, inclusive.

For comparison, the above procedure was also repeated using a composition of equal amounts by volume of the emulsion A and the dispersion C and a composition of equal amounts by volume of the emulsion B and the dispersion C, thereby obtain two dye-receiving sheets. The sheets were not satisfactory with respect to the recording densities of all cyan, magenta and yellow colors and the light fastness.

Claims

1. A dye-receiving sheet for thermal recording utilising a sublimable dye and comprising a support and a color-developing layer formed on the support, said layer being made of a dispersion of inorganic fine particles having a size below 10 μm in a binder consisting of a first resin having functional groups permitting good dye receptivity and a second resin immiscible with the first resin, the volume ratio of said second resin to said first resin being 0.1 to 10:1, whereby microscopic interstices are formed at and along boundaries between the two resins through which dye molecules can pass.

2. A dye-receiving sheet according to claim 1, wherein said first resin has a solubility parameter not smaller than 9.5.

3. A dye-receiving sheet according to claim 2, wherein the solubility parameter is not smaller than 10.0.

4. A dye-receiving sheet according to claim 1, 2 or 3 wherein said second resin has a solubility parameter not larger than 9.0.

5. A dye-receiving sheet according to claim 4, wherein the solubility parameter is not larger than 8.5.

6. A dye-receiving sheet according to any one of the preceding claims, wherein said second resin is a hydrocarbon resin, fluorine resin or silicone resin.

7. A dye-receiving sheet according to any one of the preceding claims, wherein said inorganic fine particles have an average size below 50 nm.

8. A dye-receiving sheet according to any one of the preceding claims, wherein the volume ratio of said inorganic fine particles to the total amount of the first and second resins is 0.1 to 10:1.

9. Use of a dye-receiving sheet as claimed in any one of the preceding claims in the formation of a visible image by thermal recording utilising a sublimable dye.

Patentansprüche

1. Farbaufnehmendes Blatt für thermische Aufzeichnung unter Benutzung einer sublimierbaren Farbe, mit einer Unterlage und einer auf der Unterlage ausgebildeten Farbentwicklungsschicht, wobei die Schicht aus einer Dispersion von anorganischen feinen Teilchen mit einer Größe unter 10 μm hergestellt ist in einem Binder, der aus einem ersten Harz mit Funktionsgruppen besteht, die eine gute Farbaufnahme zulassen, und einem zweiten, mit dem ersten Harz unmischnbaren Harz, wobei das Volumenverhältnis des zweiten Harzes zu dem ersten Harz zwischen 0,1 und 10:1 liegt, wodurch mikroskopische Leerstellen an und längs den Grenzen zwischen den beiden Harzen gebildet werden, durch welche die Farbmoleküle hindurchtreten können.

2. Farbaufnehmendes Blatt nach Anspruch 1, bei dem das erste Harz einen Löslichkeits-Parameter nicht kleiner als 9,5 besitzt.

3. Farbaufnehmendes Blatt nach Anspruch 2 bei dem der Löslichkeits-Parameter nicht kleiner als 10,0 ist.

4. Farbaufnehmendes Blatt nach Anspruch 1, 2 oder 3, bei dem das zweite Harz einen Löslichkeits-Parameter nicht größer als 9,0 besitzt.

5. Farbaufnehmendes Blatt nach Anspruch 4, bei dem der Löslichkeits-Parameter nicht größer als 8,5 ist.

6. Farbaufnehmendes Blatt nach einem der vorangehenden Ansprüche, bei dem das zweite Harz ein Kohlenwasserstoff-Harz, Fluor-Harz oder Silikon-Harz ist.

7. Farbaufnehmendes Blatt nach einem der vorangehenden Ansprüche, bei dem die anorganischen feinen Teilchen eine durchschnittliche Größe unter 50 nm besitzen.

8. Farbaufnehmendes Blatt nach einem der vorangehenden Ansprüche, bei dem das Volumenverhältnis der anorganischen feinen Teilchen zur Gesamtmenge des ersten und des zweiten Harzes 0,1 bis 10:1 ist.

9. Verwendung eines farbaufnehmenden Blattes nach einem der vorangehenden Ansprüche bei der Bildung eines sichtbaren Abbildes durch thermische Aufzeichnung unter Benutzung einer sublimierbaren Farbe.

Revendications

1. Une feuille réceptrice de colorant pour enregistrement thermique utilisant un colorant sublimable, qui comprend un support et une couche de développement couleur formée sur le support, ladite couche
5 étant composée d'une dispersion de fines particules inorganiques, dont la taille est en-dessous de 10 μm , dans un liant qui consiste en une première résine ayant des groupements fonctionnels permettant une bonne réceptivité au colorant et une deuxième résine, non miscible avec la première, le rapport volumique de ladite deuxième résine à ladite première résine allant de 0,1 à 10:1, grâce à quoi sont formés, aux bords et le long des limites entre les deux résines, des interstices microscopiques à travers lesquels peuvent
10 passer des molécules de colorant.
2. Une feuille réceptrice de colorant selon la revendication 1, dans laquelle ladite première résine présente un paramètre de solubilité pas plus petit que 9,5.
3. Une feuille réceptrice de colorant selon la revendication 2, dans laquelle le paramètre de solubilité n'est pas plus petit que 10,0.
- 15 4. Une feuille réceptrice de colorant selon la revendication 1, 2 ou 3, dans laquelle ladite deuxième résine présente un paramètre de solubilité pas plus grand que 9,0.
5. Une feuille réceptrice de colorant selon la revendication 4, dans laquelle le paramètre de solubilité n'est pas plus grand que 8,5.
- 20 6. Une feuille réceptrice de colorant selon l'une quelconque des revendications précédentes, dans laquelle ladite deuxième résine est une résine hydrocarbonée, une résine fluorée ou une résine silicone.
7. Une feuille réceptrice de colorant selon l'une quelconque des revendications précédentes, dans laquelle lesdites fines particules inorganiques présentent une taille moyenne située en-dessous de 50 nm.
8. Une feuille réceptrice de colorant selon l'une quelconque des revendications précédentes, dans laquelle le rapport volumique desdites fines particules inorganiques à la quantité totale des première et
25 deuxième résines va de 0,1 à 10:1.
9. Emploi d'une feuille réceptrice de colorant telle que revendiquée dans l'une quelconque des revendications précédentes, pour la formation d'une image visible par enregistrement thermique utilisant un colorant sublimable.

30

35

40

45

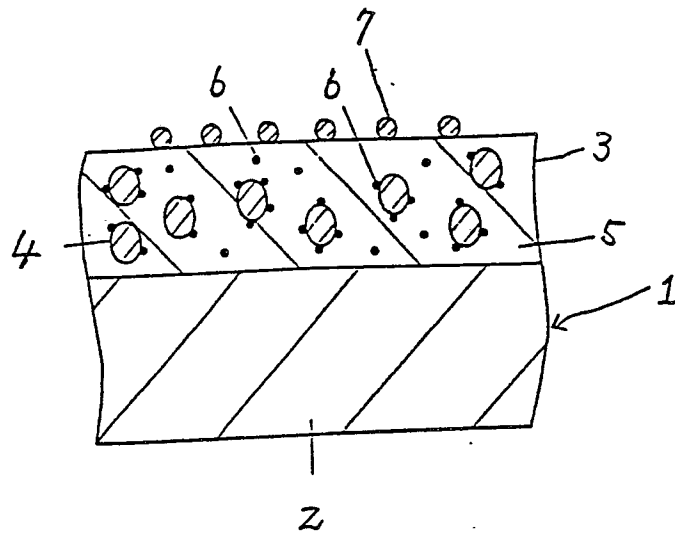
50

55

60

65

Fig. 1



PRIOR ART

Fig. 2

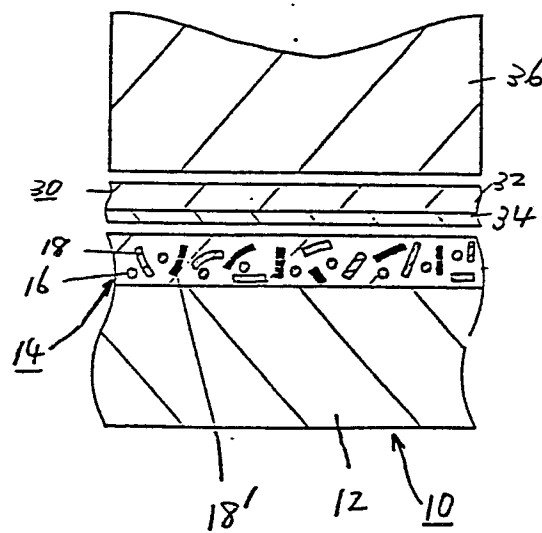


Fig. 3

